

Reactive iron supply control dominant sulfur species in the limestones of Ediacaran Doushantuo and Dengying Formations

*Fumihiko Matsuura¹, Ryoichi Nakada², Yuichiro Ueno^{3,2}, Yusuke Sawaki⁴, Masafumi Saitoh⁵, Kajitani Iori⁴, Tomohiro Usui¹

1. JAXA, 2. JAMSTEC, 3. Tokyo Tech, 4. The University of Tokyo, 5. University of Lausanne

C-S-Fe systematics in modern and ancient sedimentary systems have been intensively investigated from 1970s. The availability of reactive iron limits pyrite formation in both euxinic and non-euxinic marine sediments where sufficient metabolizable organic matter is supplied. The dominant sulfur species in the most sedimentary carbonate rocks is pyrite, though organic sulfur, a second significant sink for sulfur during early diagenesis, can be a major sulfur species exceeding the content of pyrite. Relative contribution of organic sulfur on total sulfur is controlled by the supply of reactive iron. The limestones in the Ediacaran Dengying Formation, South China have minor amount of carbonate associated iron (Fe_{carb}) concomitant with low pyrite concentration compared to the limestones and dolostones in the preceding Ediacaran Doushantuo Fm.. Given the adequate TOC content in the limestones of the Dengying Fm., pyrite content is controlled by sulfate concentration or reactive iron supply. Here we investigated species and concentration of sulfur distributed within the matrix of the limestones of the Shibantan Member in the Dengying Fm. and the Member 3 of Doushantuo Fm. by μ -XRF and S K-edge X-ray absorption near edge structure (XANES) analyses. The XANES spectra of Dengying limestone show peaks corresponding to the organic sulfur and carbonate associated sulfate (CAS), whereas the XRF analyses suggests that the organic sulfur occurs in the matrix of limestones with concentrations exceeding 100 ppm. In contrast, the XANES spectra of Doushantuo limestone indicate that the S dominantly occurs as CAS. The different characteristics observed in XANES spectra of samples collected from two Fms. suggest that sulfur cycle during the deposition of Doushantuo and Dengying Fms. were dominated by different mechanism. The abundant organic sulfur preserved in the Dengying limestone may be resulted from intense sulfurization of organic matter owing to the iron limitation during deposition. The speciation μ -XRF mapping showed that the distribution of CAS in the matrix of limestone is different between Doushantuo and Dengying limestones. The average CAS concentrations within the matrix of the two Dengying limestones are 199 ± 153 ppm and 118 ± 112 ppm with eliminating the outlier to make normal distribution. On the other hand, the average CAS concentrations within the matrix of the two Doushantuo limestones are 173 ± 37 ppm and 199 ± 53 ppm. The standard deviation of CAS concentration within the matrix of limestone in Doushantuo Fm. is much smaller than that of Dengying Fm, which shows the CAS in the limestone of the Doushantuo Fm. are distributed with small heterogeneity compared to that of the Dengying Fm. We suggest isotopic composition of a fluid possibly ocean water can be reconstructed from the limestone, in which CAS is distributed with relatively small heterogeneity, with dodging secondary vein and intense elimination of soluble sulfate.

Keywords: Doushantuo Formation, Dengying Formation, μ -XRF and S K-edge XANES, carbonate associated sulfate